

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
14 July 2005 (14.07.2005)

PCT

(10) International Publication Number
WO 2005/063390 A1

(51) International Patent Classification⁷: **B01J 35/00**,
23/89, 23/656, 23/60, 37/02, B01D 53/94

(21) International Application Number:
PCT/JP2004/018082

(22) International Filing Date:
29 November 2004 (29.11.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2003-430713 25 December 2003 (25.12.2003) JP

(71) Applicant (for all designated States except US): **NISSAN
MOTOR CO., LTD.** [JP/JP]; 2, Takara-cho, Kana-
gawa-ku, Yokohama-shi, Kanagawa 2210023 (JP).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **NAKAMURA,**
Masanori. **WAKAMATSU, Hironori.** **SUGA, Katsuo.**
SEKIBA, Toru.

(74) Agents: **MIYOSHI, Hidekazu** et al.; Toranomom Kotohira
Tower, 2-8, Toranomom 1-chome, Minato-ku, Tokyo 105-
0001 (JP).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG,
KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG,
MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH,
PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

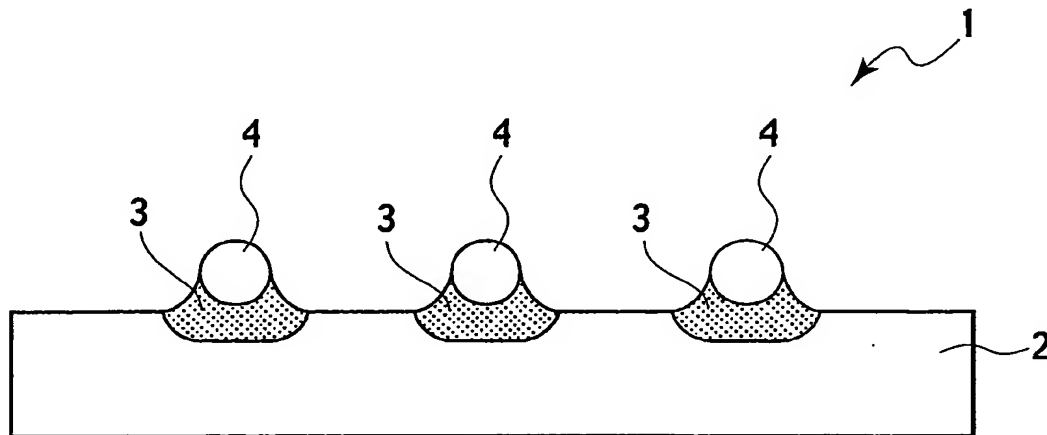
(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IS, IT, LU, MC, NL, PL, PT, RO, SE,
SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: POWDERY CATALYST, EXHAUST-GAS PURIFYING CATALYZER, AND POWDERY CATALYST PRODUCTION METHOD



(57) Abstract: In a powdery catalyst (1), a porous carrier (2) has a complex part (3) configured to hold a noble metal particle (4), the complex part being composed of a transition metal material and a constituent material of the porous carrier (2).

WO 2005/063390 A1

DESCRIPTION
POWDERY CATALYST, EXHAUST-GAS PURIFYING CATALYZER,
AND POWDERY CATALYST PRODUCTION METHOD

5 TECHNICAL FIELD

The present invention relates to a powdery catalyst, and in particular, to a powdery catalyst for purification of exhaust gases of internal combustion engine containing nitrogen oxides and the like, as well as to an exhaust-gas purifying catalyzer employing the same, and a powdery catalyst
10 production method for producing the same.

BACKGROUND ART

The regulation to exhaust gases of vehicle is spread worldwide. Exhaust gases contain hydrocarbons (HC's), carbon monoxide (CO), and
15 nitrogen oxides (NO_x), for purification of which is employed a ternary powdery catalyst in which a porous carrier, such as alumina (Al₂O₃), carries particles of (a) noble metal(s), such as platinum (Pt), palladium (Pd), and rhodium (Rh).

Noble metals provide a catalysis, which promotes associated
20 reactions as a contact reaction on an exposed surface of noble metal. For a noble metal particle, the activity of catalysis is thus proportional to the surface area. To provide a small amount of noble metal particles with a maximized catalytic activity, such particles should be prepared possibly small in size, to be high of specific surface area, and evenly dispersed over a
25 carrier, with their small sizes maintained.

Noble metal particles prepared small in size exhibit high activities in surface reaction due to great surface energy, and very unstable, so that they tend to agglomerate when brought close. In particular, Pt particles

have a remarkable tendency to sinter when heated, and even if dispersed on a carrier, they can be sintered to be large in size, with reduced catalytic activities. For vehicle-oriented catalysts, which are exposed to hot temperatures, typically within 800°C to 900°C and sometimes over 1000°C, it is difficult to hold particle size of noble metals prepared.

To control agglomeration of noble metal particles, one may reduce the surface energy. However, for such reduction to be effective, noble metal particles should be so great as 50nm or 100nm in size. Such a great size of noble metal particle fails to provide a sufficient catalytic activity.

An alternate measure is the use of an anchor for anchoring a noble metal particle on a carrier.

Japanese Patent Application Laid-Open Publication No. 59-230639 has disclosed a catalyzer in which a honeycomb substrate carries an activated alumina, which has held thereon, for carrying, particles of at least one of cerium (Ce), zirconium (Zr), iron (Fe), and nickel (Ni), at least one of neodymium (Nd), lanthanum (La), and praseodymium (Pr), as necessary, and at least one of Pt, Pd and Rh.

DISCLOSURE OF INVENTION

In this composition, particles of noble metal (Pt, Pd, Rh) fails in majority to contact with particles of transition metal (Ce, Zr, Fe, Ni), so that the majority of the former is left unanchored by the latter, and is uncontrollable against agglomeration.

The present invention has been achieved in view of such points. It therefore is an object of the invention to provide a powdery catalyst controllable against agglomeration, and excellent in durability. It also is an object of the invention to provide an exhaust gas purifying catalyzer employing such a powdery catalyst, and a powdery catalyst production

method for producing such a powdery catalyst.

To achieve the object, according to an aspect of the invention, a powdery catalyst comprises a noble metal particle, and a porous carrier provided with a complex part configured to hold the noble metal particle, the complex part comprising a composite of a transition metal material, and a constituent material of the porous carrier.

According to another aspect of the invention, an exhaust-gas purifying catalyzer comprises a powdery catalyst according to the above-noted aspect, and a substrate carrying the powdery catalyst.

According another aspect of the invention, a powdery catalyst production method comprises preparing a noble metal particle, preparing a porous carrier, and providing the porous carrier with a complex part comprising a composite of a transition metal material and a constituent material of the porous carrier, holding the noble metal particle by the complex part.

The above and further objects, features, and advantages of the invention will fully appear from the best mode for carrying out the invention, when the same is read in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a section of a powdery catalyst according to an embodiment of the invention.

FIG. 2 is a sectional view of a colloid as a fine particle according to an embodiment of the invention.

FIG. 3 is a sectional view of a colloid as a fine particle according to another embodiment of the invention.

FIG. 4 is an illustration of a powdery catalyst production method according to an embodiment of the invention.

FIG. 5 is a plan of a powdery catalyst according to an embodiment of the invention.

FIG. 6 is a plan of a powdery catalyst for comparison.

5 BEST MODE FOR CARRYING OUT THE INVENTION

There will be detailed embodiments of the invention.

(Powdery catalyst)

Description is now made of a powdery catalyst according to an embodiment of the invention. The powdery catalyst comprises a noble metal
10 particle, and a porous carrier provided with a complex part configured to hold the noble metal particle, the complex part comprising a transition metal material, and a constituent material of the porous carrier.

As illustrated in FIG. 1, in a powdery catalyst 1 according to the embodiment, a porous carrier 2 has at a surface thereof multiple complex
15 parts 3 each formed therein as a complex (or composite) of a transition metal material (i.e. one or more transition metals) and an associated part of the porous carrier 2 (i.e. one or more oxides as a constituent material thereof), whereby the transition metal material is kept stable on the porous carrier 2. Each complex part 3 has a noble metal particle 4 (i.e. particle of
20 one or more noble metals) held thereto, so that the noble metal particle 4 is hardly removed from a surface of complex part 3. The complex part 3, formed as a complex of transition metal and porous carrier, thus serves as an anchor of the noble metal particle 4, preventing agglomeration (e.g. sintering when heated) of noble metal. The noble metal particle can thus
25 be prepared in a fine size, allowing a prevented sintering, without employing a great size with which the noble metal may fail to exhibit the catalytic activity. The complex part 3 may well be a complex of simple oxide, complex oxide, or alloy.

The material to constitute an anchor may well be a metal (preferably, a transition metal) that can form a stable complex 3 with the porous carrier 2. More specifically, it is desirable for the noble metal particle 4 to be composed of one or more noble metals selected from among ruthenium, rhodium, palladium, silver, iridium, platinum, and gold, for the transition metal material to be composed of one or more transition metals selected from among manganese, iron, cobalt, nickel, copper, and zinc, and for the porous carrier 2 to be composed of one or more porous oxides selected from among alumina, silica, titanium oxide, silica alumina, and zeolite. It is more desirable for the noble metal particle 4 to be composed of platinum, for the transition metal material to be cobalt, for the porous carrier 2 to be composed of an alumina, and for the complex part 3 to be cobalt aluminate. In the case of cobalt aluminate formed by cobalt and alumina, platinum is fixed to the surface of cobalt aluminate, and kept from agglomeration.

The powdery catalyst 1 comprises the porous carrier 2, and a whole set of noble metal particles 4 dispersed thereon. The porous carrier 2 has a whole set of complex parts 3 holding a major subset of the set of noble metal particles 4, and the rest as a remaining part carrying a minor subset of the set of noble metal particles 4.

The noble metal thus reside on the complex part 3 working as an anchor. As many noble metal particles as possible, preferably 80% or more of whole noble metal particles of the powdery catalyst, are preferably located on the complex parts 3.

When noble metal and transition metal are mixed and brought as fine particles on the porous carrier 2, the noble metal preferably should have an average particle diameter within a range of 0.5nm to 20nm. An average particle diameter range under 0.5nm leads to higher surface energy, so that agglomeration is uncontrollable by anchoring only. Meanwhile, an

average particle diameter range over 20nm reduces catalytic activities. Thus, when particle diameters of noble metal carried on the porous carrier 2 ranges within 0.5nm to 20nm, preferably within 3nm to 8nm, surface energy and catalytic activities are balanced, and agglomeration seldom occurs even when heated, allowing for a maintained durability.

Noble metal particles 4 are distributed, of which state is shown by a dispersity. The dispersity means a surface to bulk ratio of a catalytic metal, which typically is proportional to an average particle diameter of the catalytic metal. After fine particles are placed on a porous carrier, this catalyst is subjected to a firing at 400°C for 1 hour, when a noble metal dispersity X1 is measured, and to a firing at 700°C for 1 hour, when a noble metal dispersity X2 is measured. Then, a ratio of X2 to X1 is checked, which preferably should be 0.7 or more. Since catalytic reactions occur substantially on the surface of noble metal, the proportion of exposed noble metal atoms at surfaces of a catalyst is essential to preparation of the catalyst. One typical method of determining the exposure is a measurement of an amount of chemical adsorption to a noble metal, followed by calculation of a dispersity of the noble metal. It is seen from the dispersity that the catalyst has a significantly decreased heat resistance, as the degree of catalysis deterioration is increased. It therefore is desirable that, between a dispersity upon preparation of a catalyst and a dispersity after endurance test, the reduction of dispersity is kept under a reference value of 0.3. If it exceeds the reference value, the catalyst may have a remarkably reduced durability.

The transition metal in the powdery catalyst preferably should be in contact with one or more elements selected from among cerium, lanthanum, zirconium, praseodymium, and neodymium. Cerium and lanthanum are preferable in consideration of catalytic activity or heat resistance of carrier,

while zirconium is preferable in consideration of heat resistance of cerium. When contacting with such elements, the transition metal has an enhanced heat resistance. Such elements may be better located at interfaces between porous carrier and transition metal, rather than in the porous carrier.

5 (Powdery catalyst production method)

Description is now made of a powdery catalyst production method according to an embodiment of the invention. The powdery catalyst production method comprises preparing a noble metal particle, preparing a porous carrier, and providing the porous carrier with a complex part
10 comprising a composite of a transition metal material and a constituent material of the porous carrier, holding the noble metal particle by the complex part.

The powdery catalyst production method preferably comprises preparing a fine particle within a size range of 0.1nm to 100nm, the fine
15 particle comprising the noble metal particle and the transition metal material, placing the fine particle on the porous carrier, and firing the porous carrier to provide the porous carrier with the complex part.

In the powdery catalyst production method, the fine particle preferably has the noble metal particle covered by particles of the transition
20 metal material.

In the powdery catalyst production method, the fine particle may preferably have a core-shell structure.

The powdery catalyst production method preferably comprises preparing a colloid comprising the fine particle covered by an organic
25 protector in a dispersion medium, and putting the porous carrier in the dispersion medium, having the colloid placed on the porous carrier.

For a complex part 3 of a porous carrier 2 and a transition metal material, to work for anchoring a noble metal particle 4, the noble metal

particle 4 should be engaged with the complex part 3, wherefor as in FIG. 2 or FIG. 3, a fine particle 13 or 23, in which noble metal and transition metal are mixed, is placed on the porous carrier 2, before a drying and a firing of entirety to form the complex part 3. The fine particle 13 or 23 is sized
5 within a range of 0.1nm to 100nm in average. Under 0.1nm, it is difficult to control particle size. Over 100nm, the fine particle may involve a greater noble metal particle than a limit size to keep a necessary catalytic activity.

In the fine particle 13, one or more noble metal particles 11 are covered or surrounded by a system of spherically arranged particles 12
10 of transition metal contacting therewith. In the fine particle 23, a spherical body 21 of noble metal or a set of noble metal particles is covered or enclosed by a hollow sphere or spherical layer 22 of transition metal contacting therewith.

The fine particle 13 or 23 is formed as part of a colloid 10 or 20 in a
15 dispersion medium, such that the particle 13 or 23 is covered by a net 14 or 24 of protective organic molecules, called "organic protector". The colloid 10 or 20 is placed on a porous carrier 2, when the porous carrier 2 is put in the dispersion medium.

The powdery catalyst production method includes: reducing, by a
20 reductant, a noble metal salt and a transition metal salt in a dispersion medium having organic protective molecules dispersed therein, forming a colloid 10 or 20 including a fine particle 13 or 23 having noble metal and transition metal mixed therein; putting a porous carrier 2 in the dispersion medium, having the colloid 10 or 20 placed on the porous carrier 2; drying
25 the porous carrier 2 with the colloid 10 or 20 placed thereon, removing an organic protector 14 or 24 therefrom to have an exposed fine particle 13 or 23 on the porous carrier 2; and firing the porous carrier 2 with the fine particle 13 or 23 (at 400°C), so that the transition metal first yields to

intrude or impregnate into depths of an extremely irregular surface region of the porous carrier 2, having an exposed noble metal particle 4 left thereon, and then forms a composite with a constituent material (e.g. oxide) of the surface region, contracting in a bowl shape with a lapse of time, thus
5 providing a complex part 3 (roots-like yielded and ring-like raised) to a surface of the porous carrier 2, having the noble metal particle 4 engaged therewith and held thereto.

The organic protective molecule may preferably be composed of one of polyvinylpyrrolidone, polyvinyl alcohol, oxalic acid, maleic acid, citric acid,
10 and the like, and a mixture thereof. The dispersion medium may preferably be one of water; an alcohol, such as methanol or ethanol; an ester, such as methyl acetate ester or ethyl acetate ester; an ether, such as diethyl ether; and a mixture thereof. The noble metal salt may preferably be one of dinitro-diamine platinum, tetraammine platinum, and the like. The
15 transition metal salt may preferably be one of cobalt acetate, cobalt nitrate, and the like. The reductant may preferably be one of hydrazine, H_2 gas, sodium borohydride, and the like.

FIG. 2 illustrates an exemplary structure of colloid 10, which has: a fine particle 13 involving a centered noble metal particle 11, and a
20 surrounding system of transition metal particles 12 contacting therewith; and an enveloping system 14 of organic protective molecules nesting the fine particle 13. This structure provides colloids 10 with a controlled tendency for agglomeration in the dispersion medium, so that they are placed on a porous carrier 2 with a sufficient dispersity, to have noble metal particles 4
25 distributed over the porous carrier 2 with a required dispersity, for the particles 4 to be sized small, as necessary for their catalytic activities to be maintained.

Preferably, the colloid including a fine particle and organic protector

should be sized 50nm or less in average, and the fine particle involving noble metal and transition metal should be sized 5nm or less in average. The fine particle may be an alloy, in its entirety or in part.

FIG. 3 illustrates an exemplary colloid 20, which has: a fine particle
5 23 of a core-shell structure involving a noble metal particle 21 as a central core, and a spherically layered transition metal particle 22 contacting therewith as an enclosing shell; and an enveloping system 24 of organic protective molecules nesting the fine particle 23. This structure allows an ensured placement of the noble metal particle 22 on a surface of deforming
10 transition metal, when fired.

Description is now made of a method of forming a fine particle of a core-shell structure (at pp 5301-5306 of J. Phys. Chem. B, 101, 1997). This method includes: putting a prescribed amount of noble metal salt in a dispersion medium having organic protective molecules dispersed therein;
15 controlling the medium to pH10 by NaOH; heating the medium at 160°C for 3 hours to obtain noble metal particles; screening the particles by a membrane filter; dispersing the particles in a water solution of ethylene glycol and ethanol; blowing a hydrogen gas into the solution to effect hydrogen adsorption for 2 hours; putting a prescribed amount of transition
20 metal salt in the solution, taking 6 hours, under a nitrogen atmosphere; and stirring the solution for 8 hours to obtain fine particles of a core-shell structure.

Fig. 4 illustrates principal steps of a powdery catalyst producing method according to an embodiment of the invention, which includes:
25 preparing colloids 20 in a dispersion medium, by using fine particles of core-shell structure formed in a described manner; putting a porous carrier 30 in the medium, having colloids 20 placed on the porous carrier 30; filtering the porous carrier 30 with colloids 20 thereon; drying the porous

carrier 30 with colloids 20 thereon, removing their organic protectors 24, so that fine particles of core-shell structure are placed on an extremely irregular surface of the porous carrier 30; and firing the porous carrier 30 with fine particles 23 thereon, at 400°C, so that shells of transition metal each yield
5 down, having lower parts thereof intruding into depths of the irregular surface, and upper parts thereof being dragged and slipping down along a periphery of the core as a noble metal particle 31 to be exposed, forming a composite with a constituent material of associated surface region of porous carrier 30, thus providing thereto a complex part 32 (roots-like yielded and
10 ring-like raised), thereby holding the noble metal particle 31 engaged therewith, with a higher efficiency than the case of fine particle 13 (FIG. 2).

FIG. 5 illustrates a microscopic view of a resultant distribution of noble metal particles 31 held on a system of substantially regular-shaped complex parts 32 substantially evenly dispersed over a principal surface of the porous carrier 30. As is apparent from this Figure, in this powdery
15 catalyst, an entire set of noble metal particles 31 has a substantially whole set thereof (at least a major subset thereof) placed on and held by an entire set of complex parts 32 of the porous carrier 30, while a very minor subset of the set of noble metal particles 31 may occasionally be placed on a
20 remaining surface portion of the porous carrier 30.

Contrary thereto, as shown in FIG. 6, in a powdery catalyst produced by a conventional method, a minor subset of an entire set of noble metal particles 41 is simply placed on a subset of an entire set of irregular-shaped complex parts 42 of a porous carrier 40, and a major subset
25 of the entire set of noble metal particles 41 is uncontrollably dispersed on a remaining surface portion of the porous carrier 40.

According to the embodiment described, particles of noble metal and transition metal are mixed in the form of a fine particle of core-shell

structure sized within a prescribed range, and a porous carrier with the fine particle placed thereon is fired, so that the porous carrier has a complex part formed by a constituent material thereof and the transition metal, which provides an anchoring effect to have noble metal particles
5 individually held thereto.

(Powdery catalyst)

Description is now made of an exhaust-gas purifying catalyzer according to an embodiment of the invention. The exhaust-gas purifying catalyzer comprises a powdery catalyst according to a described embodiment,
10 and a substrate carrying the powdery catalyst.

The exhaust-gas purifying catalyzer may preferably contain a total quantity of noble metal particles not exceeding 0.7g per 1 L of a volume of the substrate. It was difficult for a conventional exhaust-gas purifying catalyzer to achieve a sufficient catalytic activity with a total quantity of
15 noble metal particles not exceeding 0.7g per 1 L of a substrate volume, due to unavoidable agglomeration of noble metal particles.

However, according to the embodiment in which agglomeration of noble metal particles is controlled by an anchoring effect acting on individual noble metal particles, it is possible to achieve a sufficient
20 catalytic activity with a total quantity of noble metal particles not exceeding 0.7g per 1 L of a substrate volume.

Examples

Specific examples of powdery catalyst according to embodiments of the invention will be described below, as Example 1 through Example 4, and
25 Comparative Example 1, to discuss the effect by kinds of materials used.

<Preparation of Specimens>

(Example 1)

Firstly, delivered into a mixed dispersed solution including

water:ethanol=1:1 were 55 mmol of polyvinylpyrrolidone, 1.54 mmol of dinitro-diamine platinum, and 7.7 mmol of cobalt nitrate, followed by stirring. Next, added thereto was hydrazine for reduction, thereby obtaining a dispersed solution of platinum-cobalt mixed fine particles having an average particle diameter of 3.2nm. Delivered thereinto was 100g of alumina having a specific surface area of 200m²/g and an average pore diameter of 20nm, followed by stirring and by drying at 120°C overnight. Thereafter, firing was conducted at 400°C for 1 hour, thereby obtaining a powdery catalyst.

10 (Example 2)

Delivered into ethylene glycol were 55 mmol of polyvinylpyrrolidone and 1.54 mmol of dinitro-diamine platinum, and NaOH was dropped into it while stirring to achieve pH=10, followed by heating at 160 °C for 3 hours, thereby obtaining platinum fine particles having an average particle diameter of 2.3nm. Next, the obtained platinum fine particles were washed by a membrane filter, and they were delivered into a solution including water:ethylene glycol:ethanol at 1:1:1, followed by bubbling of hydrogen gas for 2 hours, thereby adsorbing the hydrogen gas onto a surface of platinum. Thereafter, cobalt nitrate was delivered, followed by stirring for 5 hours, thereby obtaining platinum fine particles coated by cobalt. The obtained fine particles had an average particle diameter of 3.4nm. Delivered into this solution was 100g of alumina having a specific surface area of 200m²/g and an average pore diameter of 20nm, followed by stirring and by drying at 120°C overnight. Thereafter, firing was conducted at 400°C for 1 hour, thereby obtaining a powdery catalyst.

(Example 3)

Impregnated into the powder obtained in Example 1 were cerium acetate, lanthanum acetate, and zirconium acetate at 8.5 wt%, 5.5 wt%, and

6 wt%, respectively, when calculated as oxides relative to the powder, followed by drying at 120°C overnight and by firing at 400°C for 1 hour. This was a powder A. Next, impregnated into 100g of alumina having a specific surface area of 200m²/g and an average pore diameter of 20nm, was
5 zirconium acetate at 5 wt% when calculated as oxide relative to the alumina, followed by drying at 120°C overnight and by firing at 900°C for 4 hours. Impregnated into it was rhodium nitrate in a manner to achieve 0.3 wt%, followed by drying at 120°C overnight and by drying at 400°C for 1hour. This was a powder B. Charged into a porcelain ball mill were 175g of the
10 powder A, 62.5g of the powder B, 12.5g of alumina sol, 230g of water, and 20g of nitric acid, followed by mixing and grinding, thereby obtaining a catalyst slurry. The obtained catalyst slurry was coated on a monolithic carrier made of cordierite (0.119L, 400 cell), and an excessive slurry within cells was removed by airflow, followed by drying at 120°C and firing
15 thereafter at 400°C for 1 hour, thereby obtaining a powdery catalyst having a coating layer of 200.0g/L.

(Example 4)

The same procedure as Example 3 was conducted, except that the powder obtained in Example 2 was used as the powder A.

20 (Comparative Example 1)

Carried on 100g of alumina having a specific surface area of 200m²/g and an average pore diameter of 20nm was dinitro-diamine platinum in a manner to achieve 0.6 wt%, followed by drying at 120°C overnight and firing thereafter at 400°C for 1 hour. Further, carried on 100g of alumina
25 having a specific surface area of 200m²/g and an average pore diameter of 20nm was cobalt nitrate in a manner to achieve 3 wt%, followed by drying at 120°C overnight and firing thereafter at 400°C for 1 hour. The same procedure as Example 3 was conducted except that the same amounts of

these powders were used to provide a mixed powder A.

Herein, the specimens obtained by the above specimen adjustment were evaluated by the following manner.

<Durability Test>

5 Durability test of powdery catalyst was conducted by firing each of obtained powdery catalysts at 700°C for 1 hour in an oxidizing atmosphere.

<Evaluation Manner of Conversion Ratio>

Based on a model gas shown in Table 1, there was obtained a 50%-conversion temperature during elevation from room temperature to
10 400°C at 10°C/min. Further, there was obtained a conversion ratio at 400°C.

Table 1

Reaction Gas Composition	
Gas composition	Stoichiometric
Z value(-)	1.000
A/F(-)	14.5
NO (ppm)	1,000
CO(%)	0.6
H ₂ (%)	0.2
O ₂ (%)	0.6
CO ₂ (%)	13.9
HC(ppmC)	1665
H ₂ O(%)	10
N ₂ (balance)	remainder

<Measuring Method of Noble Metal Dispersity>

15 Used for measurement of noble metal dispersity was a metal dispersity measuring device BEL-METL-3 manufactured by Bel Japan, Inc., and measurement was conducted in accordance with the following procedure. Each specimen was heated to 400°C at 10°C/min, and then oxidation

treatment was conducted for 15 minutes at 400°C in gas flow of 100% O₂. Purging was then conducted for 5 minutes by 100% He gas, and a reduction treatment was conducted at 400°C for 15 minutes in a gas of 40% H₂/balance He. Thereafter, the temperature was lowered down to 50°C in a gas flow of 100% He. Then, 10% cobalt/ balance He gas was pulsedly flowed in, to obtain a noble metal dispersity based on an adsorbed cobalt amount, in accordance with the following formula.

(Mathematical Formula 1)

$$\text{Dispersity (\%)} = \frac{(100 \times [\text{atomic weight of carried metal}] \times [\text{unit adsorbed amount}])}{(22414 \times [\text{stoichiometric ratio}] \times [\text{content rate of carried metal}])}$$

*unit adsorbed amount [cm³/g]=total adsorbed amount/ specimen weight

10 <Measurement of particle diameters of noble metal and transition metal>

Evaluation was performed based on TEM-EDX measurement, by scraping down a catalyst layer from each exhaust-gas purifying catalyzer obtained by the above specimen preparation. The measurement was conducted by using an HF-2000 manufactured by Hitachi, Ltd., at an accelerating voltage of 200kV and a cutting condition of ordinary temperature. The measuring method was to embed the powdery catalyst in an epoxy resin, and to prepare an ultra-thin slice by an ultra-microtome after the epoxy resin had cured. Dispersed states of various crystal grains were investigated by a transmission electron microscope (TEM), by using the slice. Contrasted (shadow) parts in the obtained image were focused to determine metal kinds, to measure particle diameters (Ar and Br) of the metals.

<Measurement of Conversion Ratio>

Qualitative, quantitative and state analyses of the elements of each specimen were conducted by X-ray photoelectron spectroscopy (XPS). Measurement was conducted by fixing the specimen on an indium foil while
5 adopting a composite-type surface analyzing apparatus manufactured by PHI, under the condition that the X-ray source was Al-K α ray (1486.6 eV, 300W), the photoelectron extraction angle was 45° (measurement depth of 4nm), and the measuring area was 2-mm \times 0.8-mm. Upon measurement, hydrogen (hydrogen 0.2%/nitrogen) as one of compositions of exhaust gas
10 was exposed at 400°C \times 10 minutes within a pretreatment chamber attached to the XPS apparatus, and then the XPS measurement was performed.

Based on the results obtained from the TEM-EDX measurement, the platinum powdery catalyst obtained in Example 1 had an average particle diameter of 4.8nm, and the platinum powdery catalyst obtained in Example
15 2 had an average particle diameter of 4.6nm. Note that each of specimens obtained in Example 1 and Example 2 had a platinum carrying concentration of 0.3 wt% and a cobalt carrying concentration of 1.5 wt%. Further, in Example 1 and Example 2, cobalt was compositeed with alumina and brought into cobalt-aluminates. As shown in a schematic view
20 of FIG. 5, most of platinum fine particles were existent on the cobalt-aluminates, respectively.

Following Table 2 shows a 50%-conversion-ratio temperature °C after endurance (after firing at 700°C) and a conversion ratio % at 400°C after endurance (after firing at 700°C). Table 3 shows a dispersity (X1) at
25 the time of preparation of catalyst (after firing at 400°C), a dispersity (X2) after endurance (after firing at 700°C), and X2/X1.

In Examples 3, 4 and Comparative Example 1, Comparative Example 1 had a higher 50%-conversion-ratio temperature °C and a lower

value for a conversion ratio % at 400°C after endurance (after firing at 700°C), as compared with Examples 3, 4. Further, although its dispersity (X1) at the time of preparation of catalyst was high, its dispersity (X2) after endurance (after firing at 700°C) was considerably lowered. From these results, the X1/X2 of Comparative Example 1 had a smaller value as compared with Examples 3, 4.

Table 2

	50%-conversion-ratio temperature(°C) after endurance			Conversion ratio(%) at 400°C after endurance		
	HC	CO	NOx	HC	CO	NOx
Ex. 3	282	253	265	99	99	99
Ex. 4	275	241	254	99	99	99
Com. Ex. 1	295	268	277	91	95	90

Table 3

	Dispersity (X1) at preparation of catalyst (after firing at 400°C)	Dispersity (X2) after endurance (after firing at 700°C)	X2/X1
Ex. 3	51	37	0.73
Ex. 4	52	42	0.81
Com. Ex. 1	72	3	0.04

In this way, although the anchoring effect was exhibited when the fine particles created by mixing noble metal and transition metal were carried by alumina, such an anchoring effect was not obtained when the noble metal and transition metal were separately carried, thereby leading to

a deteriorated dispersity.

Based on the above, since the noble metal and transition metal are mixed to form fine particles having an average particle diameter of 0.1nm to 100nm and the fine particles are provided in the core-shell structures so that the transition metal forms the composite together with the porous oxide, it becomes possible to cause the porous oxide to firmly carry the noble metal thereon by virtue of the anchoring effect. Further, since agglomeration of noble metal particles is restricted by the anchoring effect, it becomes possible to obtain a catalyst having a higher dispersity and to firmly carry the fine particles on the porous oxide.

The present invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the present invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

INDUSTRIAL APPLICABILITY

According to the present invention, there is provided a powdery catalyst having noble metal particles controlled against agglomeration, with excellent durability.

CLAIMS:

1. A powdery catalyst comprising:
a noble metal particle; and
a porous carrier provided with a complex part configured to hold the
5 noble metal particle, the complex part comprising a composite of a
transition metal material, and a constituent material of the porous carrier.
2. The powdery catalyst as claimed in claim 1, comprising:
a set of noble metal particles; and
the porous carrier comprising:
10 a set of complex parts holding a major subset of the set of
noble metal particles; and
a remaining part carrying a minor subset of the set of noble
metal particles.
3. The powdery catalyst as claimed in claim 1, wherein
15 the noble metal particle comprises one of ruthenium, rhodium,
palladium, silver, iridium, platinum, and gold,
the transition metal material comprises one of manganese, iron,
cobalt, nickel, copper, and zinc, and
the constituent material comprises one of an alumina, a silica, a
20 titanium oxide, a silica alumina, and a zeolite.
4. The powdery catalyst as claimed in claim 1, wherein the noble
metal particle is sized within a range of 0.5nm to 20nm.
5. The powdery catalyst as claimed in claim 4, wherein, between a
dispersity X1 of noble metal particles after a one-hour firing at 400°C and a
dispersity X2 of noble metal particles after a one-hour firing at 700°C, a
25 ratio X2/X1 of the dispersity X2 to the dispersity X1 is 0.7 or more.
6. The powdery catalyst as claimed in claim 1, wherein
the noble metal particle comprises platinum,

the transition metal material comprises cobalt, and
the complex part comprises cobalt aluminate.

7. The powdery catalyst as claimed in claim 1, wherein the complex
part comprises one of cerium, lanthanum, zirconium, praseodymium, and
5 neodymium, contacting with the transition metal material.

8. An exhaust-gas purifying catalyzer comprising:
a powdery catalyst according to claim 1; and
a substrate carrying the powdery catalyst.

9. The exhaust-gas purifying catalyzer as claimed in claim 8,
10 containing a total quantity of noble metal particles not exceeding 0.7g per 1
L of a volume of the substrate.

10. A powdery catalyst production method comprising:
preparing a noble metal particle;
preparing a porous carrier; and
15 providing the porous carrier with a complex part comprising a
composite of a transition metal material and a constituent material of the
porous carrier, holding the noble metal particle by the complex part.

11. The powdery catalyst production method as claimed in claim 10,
comprising:
20 preparing a fine particle within a size range of 0.1nm to 100nm, the
fine particle comprising the noble metal particle and the transition metal
material;

placing the fine particle on the porous carrier; and
firing the porous carrier to provide the porous carrier with the
25 complex part.

12. The powdery catalyst production method as claimed in claim 11,
wherein the fine particle has the noble metal particle covered particles of
the transition metal material.

13. The powdery catalyst production method as claimed in claim 11, wherein the fine particle has a core-shell structure.

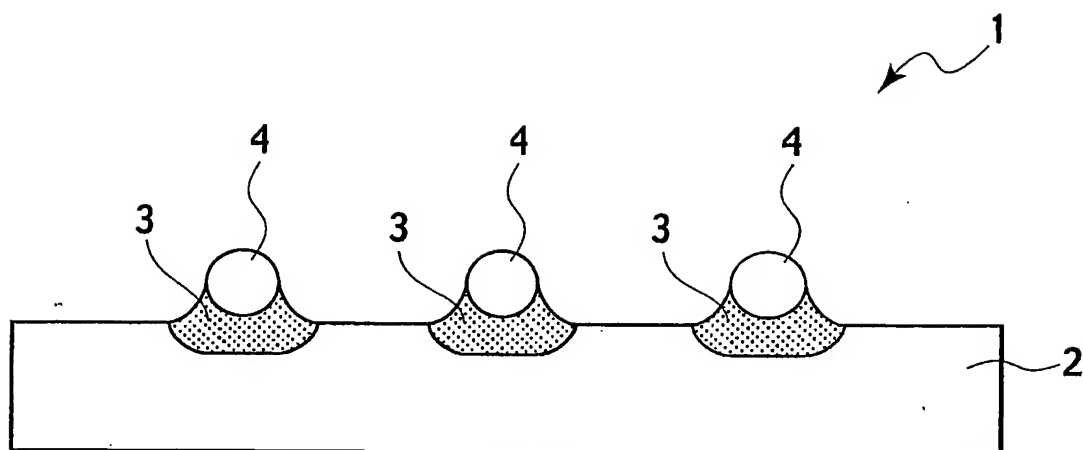
14. The powdery catalyst production method as claimed in claim 11, comprising:

5 preparing a colloid comprising the fine particle covered by an organic protector in a dispersion medium; and

 putting the porous carrier in the dispersion medium, having the colloid placed on the porous carrier.

1/4

FIG. 1



2/4

FIG. 2

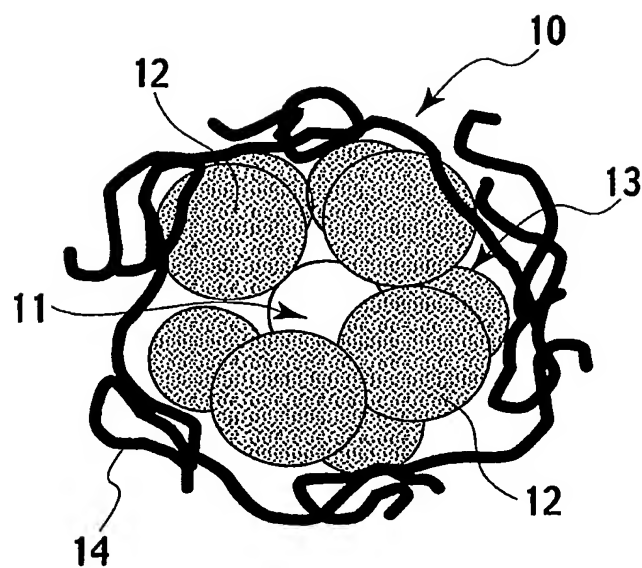
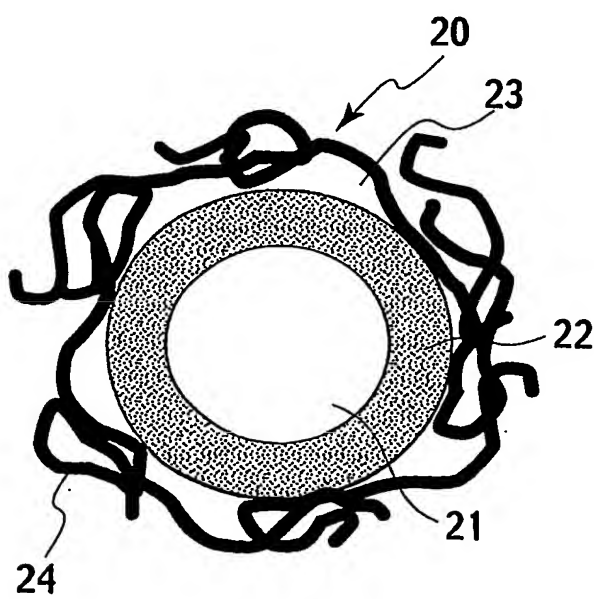
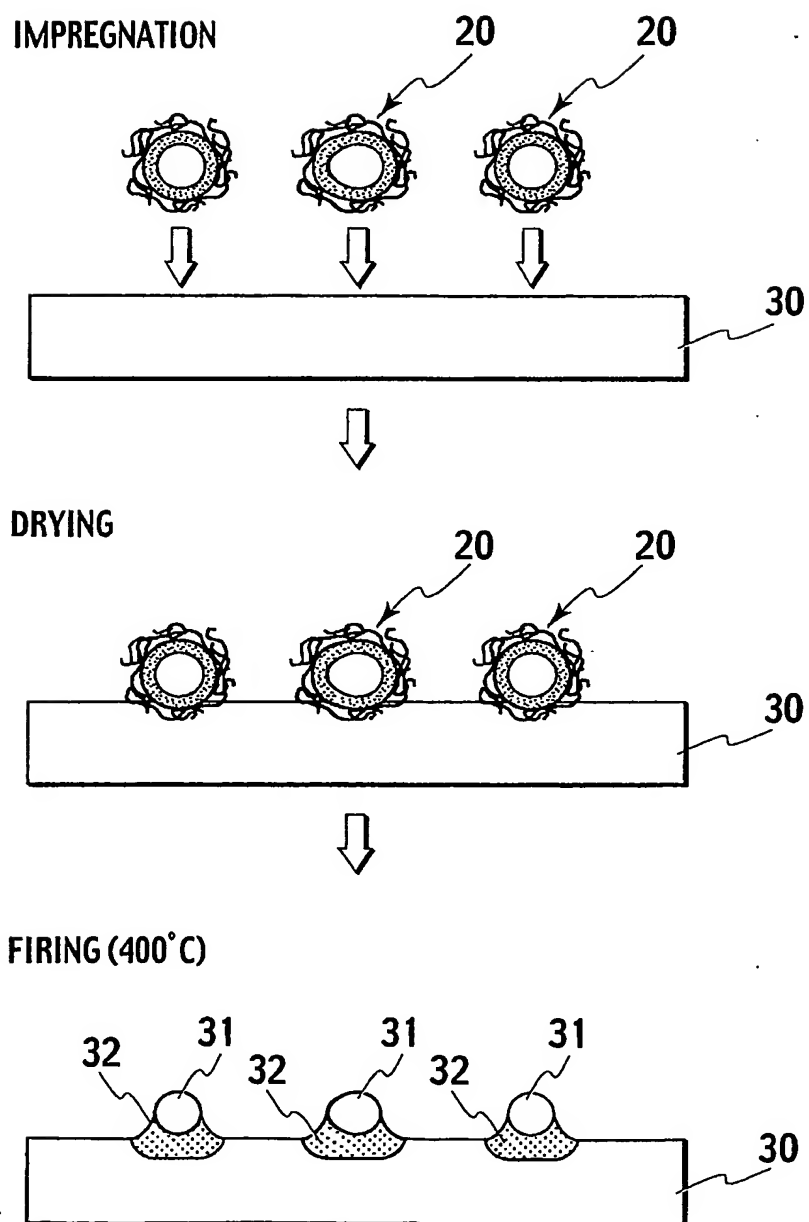


FIG. 3



3/4

FIG. 4



4/4

FIG. 5

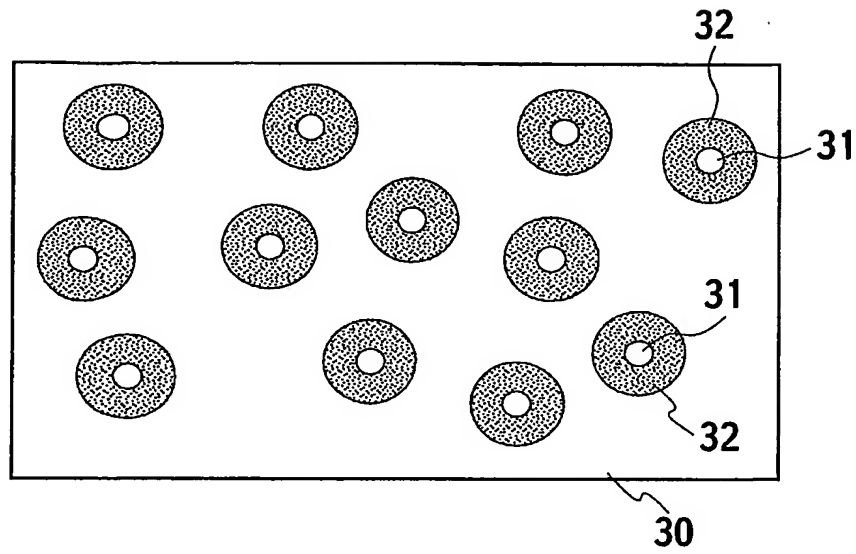
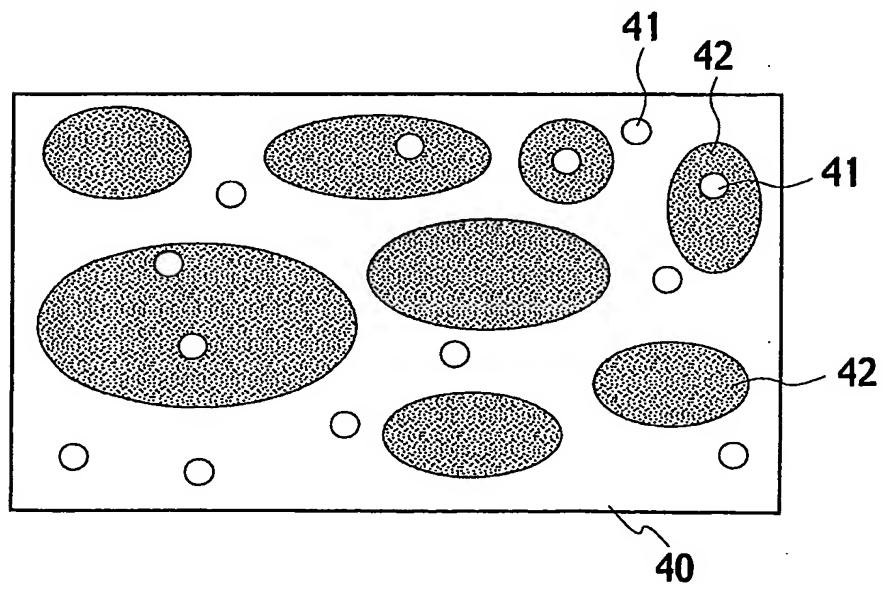


FIG. 6



INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP2004/018082

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J35/00 B01J23/89 B01J23/656 B01J23/60 B01J37/02
B01D53/94

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01J B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 13, 5 February 2001 (2001-02-05) & JP 2000 296339 A (TOYOTA MOTOR CORP), 24 October 2000 (2000-10-24) abstract	1-14
X	WO 95/32790 A1 (ALLIEDSIGNAL ENVIRONMENTAL CATALYSTS) 7 December 1995 (1995-12-07) the whole document	1-14
X	EP 1 043 065 A (TOYOTA JIDOSHA KABUSHIKI KAISHA) 11 October 2000 (2000-10-11) the whole document	1,2,4,5, 7,8, 10-12,14
	----- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *G* document member of the same patent family

Date of the actual completion of the international search

1 February 2005

Date of mailing of the international search report

08/02/2005

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Zuurdeeg, B

INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP2004/018082

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 516 741 A (GASCOYNE ET AL) 14 May 1996 (1996-05-14) examples 7,8,12-17	1-5,8, 10-12,14
P,X	----- PATENT ABSTRACTS OF JAPAN vol. 2003, no. 12, 5 December 2003 (2003-12-05) & JP 2004 082000 A (TOYOTA MOTOR CORP), 18 March 2004 (2004-03-18) abstract -----	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/JP2004/018082

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 2000296339	A	24-10-2000	NONE	
WO 9532790	A1	07-12-1995	DE 69517687 D1 DE 69517687 T2 EP 0762926 A1 JP 10501172 T US 5977012 A	03-08-2000 28-12-2000 19-03-1997 03-02-1998 02-11-1999
EP 1043065	A	11-10-2000	DE 69826030 D1 EP 1043065 A1 US 6440378 B1 WO 9932223 A1	07-10-2004 11-10-2000 27-08-2002 01-07-1999
US 5516741	A	14-05-1996	AT 109025 T DE 69103080 D1 DE 69103080 T2 EP 0457480 A1	15-08-1994 01-09-1994 01-12-1994 21-11-1991
JP 2004082000	A	18-03-2004	NONE	